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By Earl H. Pampeyan

Introduction

The mineral buddingtonite, named after A.F. Buddington, long-time professor of petrology at Princeton University, was first identified at the Sulfur Bank mine in Lake County, California (Erd and others, 1964). The ammonium feldspar was recognized in Menlo Park, California, in 1964 by the author, with Erd's help, shortly before publication of the original description of the new mineral (Geological Survey Research, 1964). Subsequently, buddingtonite has been widely recognized in hydrothermal mineral deposits and has been used in remote-sensing applications by the mineral industry (Krohn and others, 1993; Felzer and others, 1994). Buddingtonite also has been identified in the Phosphoria Formation (Gulbrandsen, 1974) and in oil shales of the Green River Formation (Oh and others, 1993). This paper briefly describes the geologic setting and mineralogy of the occurrences of buddingtonite and other ammonium-bearing minerals in the vicinity of Menlo Park.

Geographic and Geologic Setting

The Palo Alto 7½-minute quadrangle straddles the San Mateo-Santa Clara County boundary, about 55 km south of San Francisco (fig. 1). The quadrangle includes hills and foothills of the Santa Cruz Mountains and gently sloping flatlands leading to San Francisco Bay. The southwest corner of the quadrangle is cut by the San Andreas Fault, which separates foothills and flatlands on the northeast side from steep, densely wooded slopes on the southwest side. The foothills and flatlands have been developed for residential and light industrial uses, and the steeper hills have been developed for low-density residential use. Stanford University is situated near the center of the quadrangle.

The geologic setting of a part of Menlo Park is shown in figure 2. Folded and faulted Eocene (Whiskey Hill Formation) and Miocene (Ladera Sandstone) sandstones and claystones, locally overlain by Quaternary surficial deposits, are present in this area (Pampeyan, 1970, 1993). Fold axes in the sedimentary rocks trend northwest, approximately parallel to the San Andreas Fault, and dips range from moderate to steep. The Eocene strata are penetrated by a "diapir" of serpentinite, along the axis of an anticlinal fold, and by a dike with the appearance of hydrothermally altered rhyolite. In addition to the altered dike, igneous rocks in the form of basalt flows underlie the Miocene beds nearby, and a diatomaceous vitric tuff near the top of the exposed Miocene Monterey Formation is present beyond the southeast corner of figure 2 (loc. 8, fig. 1). The basalt flows are believed to have issued from a vent about 4.5 km southeast of the altered rhyolite dike (loc. 10, fig. 1); the source of ammonia-bearing rhyolitic glass shards comprising the vitric tuff is unknown but may be related to the altered dike.

The altered rhyolite dike strikes northeast, cutting across bedding in the Eocene Whiskey Hill Formation. Its exposed length is approximately 58 m, and it ranges in width from 8 to 16 m, standing as a wall up to 1.5 m above the surrounding sedimentary rocks (fig. 3). The host rock of the southern half of the dike is montmorillonitic claystone and the northern half feldspathic sandstone, the northernmost end of the dike consisting of a mixture of silicified sandstone and

dike rock. The dike rock has an aphanitic to microcrystalline texture and ranges in color from light- to medium-gray (N7 to N4) (Goddard, 1963) where silicified and hard, and is white, yellowish-gray (5Y8/1), and pale olive (10Y6/2) where clayey and soft. In places the dike rock is stained moderate red (5R5/4) to dusky red (5R3/4) by oxidized iron sulfides. Vertical flow-banding generally flares outward near the present upper surface of the dike; in some places flow-banding is emphasized by dark streaks of fresh iron sulfides. Parts of the dike's upper surface are covered by "scabs" of silicified breccia composed of sandstone, claystone and rhyolite. These scabs of breccia have protected the softer underlying altered rocks from erosion. The dike is fractured and the fractures are either filled (silicified breccia) or lined (soft dike rock) with jarosite and ammoniojarosite. The entire dike has been thoroughly affected by ammonium alteration so that all the original feldspars have been converted to buddingtonite.

Mineralogy

Buddingtonite in the rhyolite dike is a rather nondescript and soft amorphous material resembling clay. Chemically and mineralogically it is identical to the type buddingtonite from the Sulfur Bank mine (Erd and others, 1964). No visible crystalline buddingtonite was found in the dike; the enclosing sandstone, however, contains what appear to be buddingtonite pseudomorphous after detrital feldspar grains.

Only small aggregates of quartz crystals in a cloudy groundmass are visible in thin-sections of dike rock, but x-ray diffraction patterns show that the rock is composed principally of buddingtonite and quartz. The proportions of these minerals vary, judging by the intensities of their peaks, from sample to sample, but no attempt was made to estimate an average buddingtonite-to-quartz ratio.

Medium- to coarse-grained feldspathic sandstones in and near the dike exhibit varying degrees of alteration, the cations of the detrital feldspar having been partly to wholly replaced by NH_4 . Claystone in and adjacent to the dike also contains ammonia, but according to x-ray diffraction patterns there is little buddingtonite in the clay. The claystones are expansive and contain a substantial amount of Na-montmorillonite. Very likely the ammonia is held by the montmorillonite as a substitute for sodium. Jarosite is common and occurs as discrete layers of dense amorphous yellowish-gray (5Y7/2) to pale-olive-green (10Y5/2) material up to 10 mm thick along fractures in the dike and filling fractures in the silicified breccia. The contact between jarosite and buddingtonite is sharp and coincides with a change in color and texture, the jarosite generally being more compact than the white to yellowish-gray buddingtonite. Ammoniojarosite occurs in the dike both as small honey-colored crystals and as greenish-yellow (10Y8/2) amorphous material filling fractures. The relative amounts of jarosite and ammoniojarosite—and their interrelations—are unknown, but x-ray diffraction patterns of the amorphous material show better-developed ammoniojarosite peaks, suggesting that ammoniojarosite predominates.

Minor cinnabar was found at two places along the west-central edge of the dike as fracture fillings and also disseminated through the buddingtonite. Under the microscope cinnabar crystals are visible both on and in crystalline quartz and as crystals and clots in ammoniojarosite and jarosite. Though most commonly associated with buddingtonite, some cinnabar is present in the siliceous matrix of the capping silicified breccia.

Pyrite and marcasite(?) are common in the dike, especially in the silicified breccia. These sulfides are disseminated throughout the dike in small sheaf-like aggregates, usually elongated parallel to relict flow structures, and also along bedding planes in sandstone breccia fragments. In a few places, the sulfides have been oxidized and have leached out, leaving a rusty stain.

Other minerals present in the dike rock, but in lesser amounts, are gypsum, alunite, and niter (table 1). These minerals were identified in several samples by R.C. Erd (oral commun., 1964). An ammonium analog of muscovite was also recognized in samples from Menlo Park by Erd in 1964. Minerals, or evidence of minerals, visible in individual samples or as individual occurrences in the dike rock include oily hydrocarbons in quartz-lined vugs in the silicified breccia, similar to oily hydrocarbons found in many California quicksilver deposits; anatase, noted only in x-ray diffraction patterns; pyrrhotite(?), noted as negative crystals in buddingtonite; chalcopyrite, noted as iridescent brass-colored grains in a few clots of pyrite; covellite(?), noted as a few blue metallic grains in the silicified breccia; and carnotite, noted as two small green crystals in buddingtonite. At least some of the minerals in this assemblage are also associated with the Sulfur Bank buddingtonite, namely alunite, ammoniojarosite, anatase, cinnabar, gypsum, hydrocarbons, marcasite, pyrite, and pyrrhotite. These associations probably are genetic because of the type of alteration involved.

Other Localities

After buddingtonite was identified in the dike rock, samples of wall rock and similar rocks from other localities were tested for ammonia and buddingtonite (table 2). The ammonium alteration has affected detrital feldspars in the enclosing sedimentary rocks, as a "halo" of buddingtonite appears in the feldspathic sandstones for a distance of at least 245 m along strike (localities 2 and 3, fig. 2). Owing to the discontinuous outcrop of soft Eocene claystones it was difficult to define the extent of ammonium alteration, but samples from localities 4, 5, 6, and 7 (fig. 2) also gave positive ammonia reactions and contained some buddingtonite. In addition to these occurrences, strong positive reactions for ammonia came from samples of a Miocene diatomaceous vitric tuff (loc. 8, fig. 1) and a mid-Miocene fine-grained clayey sandstone (loc. 9, fig. 1). At localities 8 and 9, the NH_4 is concentrated in glass shards of the tuff and in the clayey binder of the sandstone.

The presence of small amounts of cinnabar in the dike and the association of cinnabar and buddingtonite at the type locality (Erd and others, 1964) suggest that buddingtonite might be common and could possibly serve as an indicator of mercury deposits. Therefore, available samples of altered rocks from two nearby mercury districts were examined (table 2). Samples of altered rock from two localities in the Mount Diablo district (Pampeyan, 1964) contained ammonia, but buddingtonite was not present in x-ray diffraction patterns. The NH_4 in the Mount Diablo district is held in clay minerals of a bleached greywacke specimen and in the sericite of an altered rhyodacite specimen. Some of the original feldspars of the greywacke possibly were altered to buddingtonite but were masked by an abundance of unaltered feldspar. Samples of volcanic rocks from the New Almaden district (Bailey and Everhart, 1964) gave negative results.

Conclusion

A rhyolite(?) dike in the Palo Alto quadrangle has been subjected to hydrothermal ammonia alteration, probably related to a period of late(?) Miocene volcanism. This alteration has produced buddingtonite and ammoniojarosite—and possibly ammonium montmorillonite and ammonium mica—in the dike and adjacent rocks. Ammonium alteration in the enclosing sedimentary rocks is marked by the presence of ammonia minerals as far as 5.5 km from the dike. The presence of cinnabar and buddingtonite in the dike and indications of ammonium alteration in the Mount Diablo district suggest a relationship between mercury deposits and ammonium alteration similar to that described by White and Roberson (1962) and Erd and others (1964) at the Sulfur Bank mine, type locality for buddingtonite. Examination of altered rocks in other mercury districts may uncover other localities for buddingtonite or, conversely, recognition of ammonium alteration may possibly serve as an indicator of mercury mineralization.

More recent studies of hydrothermal mineral systems indicate that buddingtonite is present in many hydrothermal mineral deposits and can be detected by remote-sensing techniques (Krohn and others, 1993; Felzer and others, 1994).

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Figures

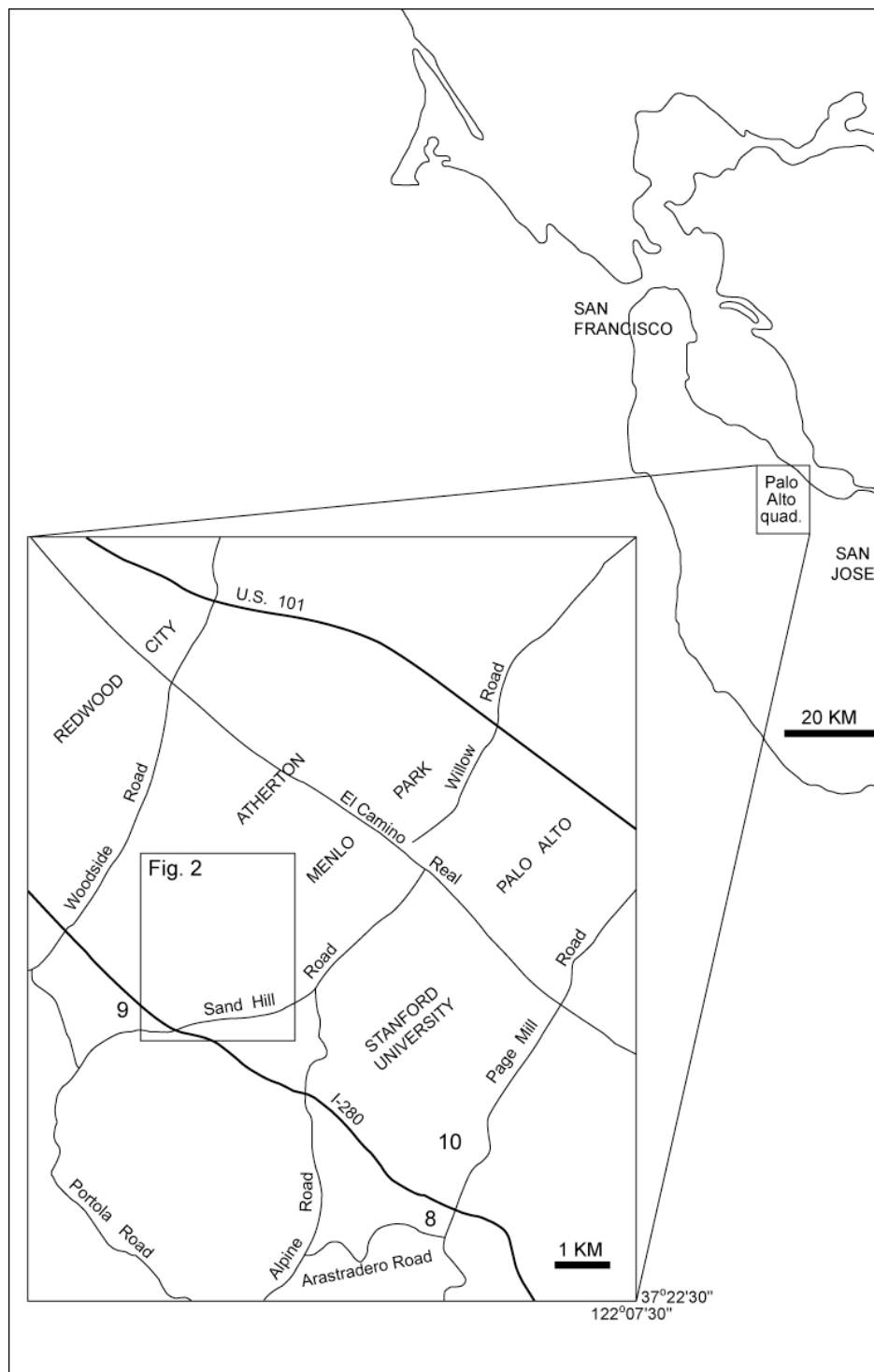


Figure 1. Index map showing location of the Palo Alto 7½' quadrangle, figure 2, and outlying sample localities noted in the text.

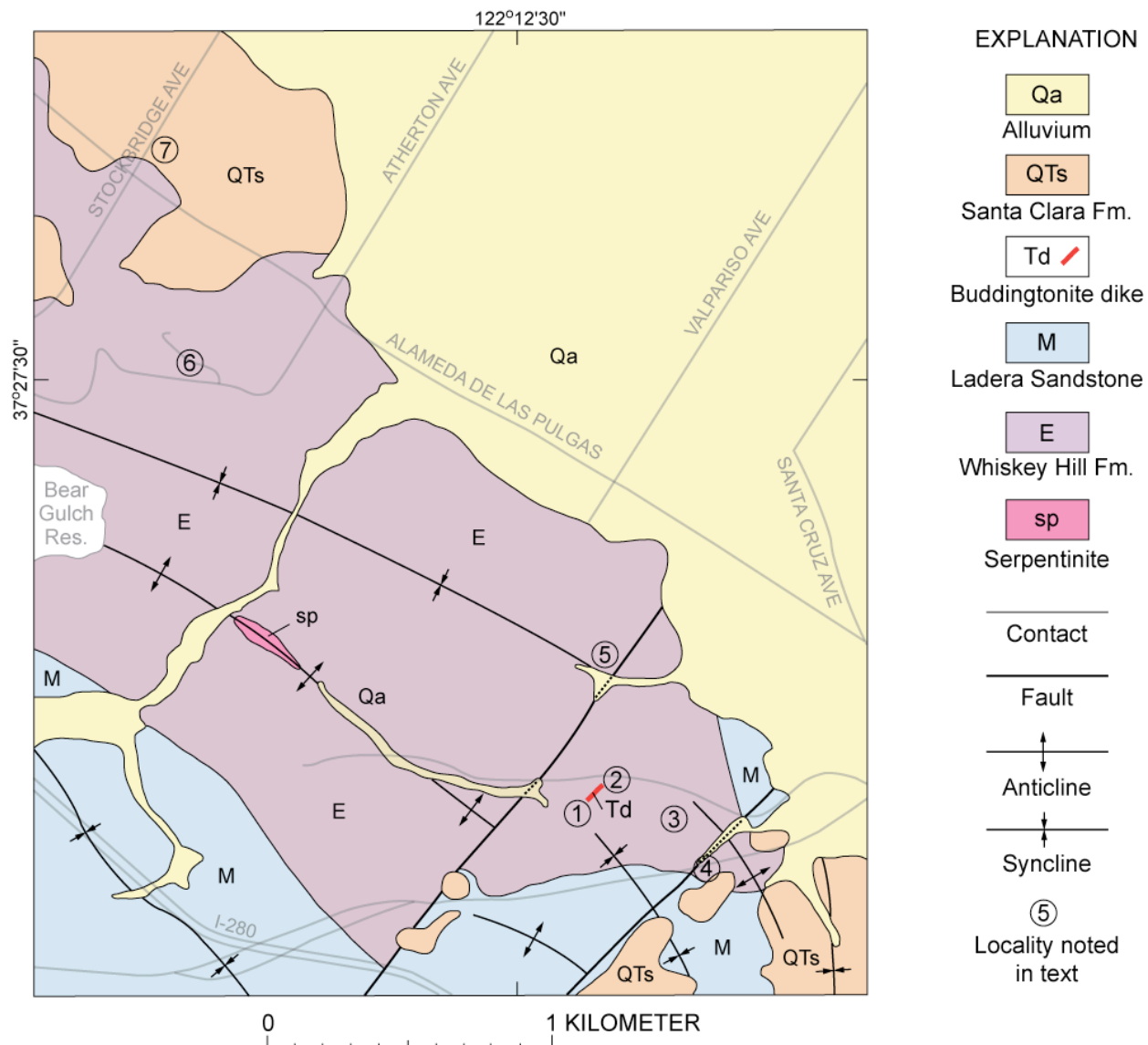


Figure 2. Geologic map of the area surrounding the buddingtonite dike, Menlo Park, California. Sample localities are noted. See Pampeyan (1993) for more detail.

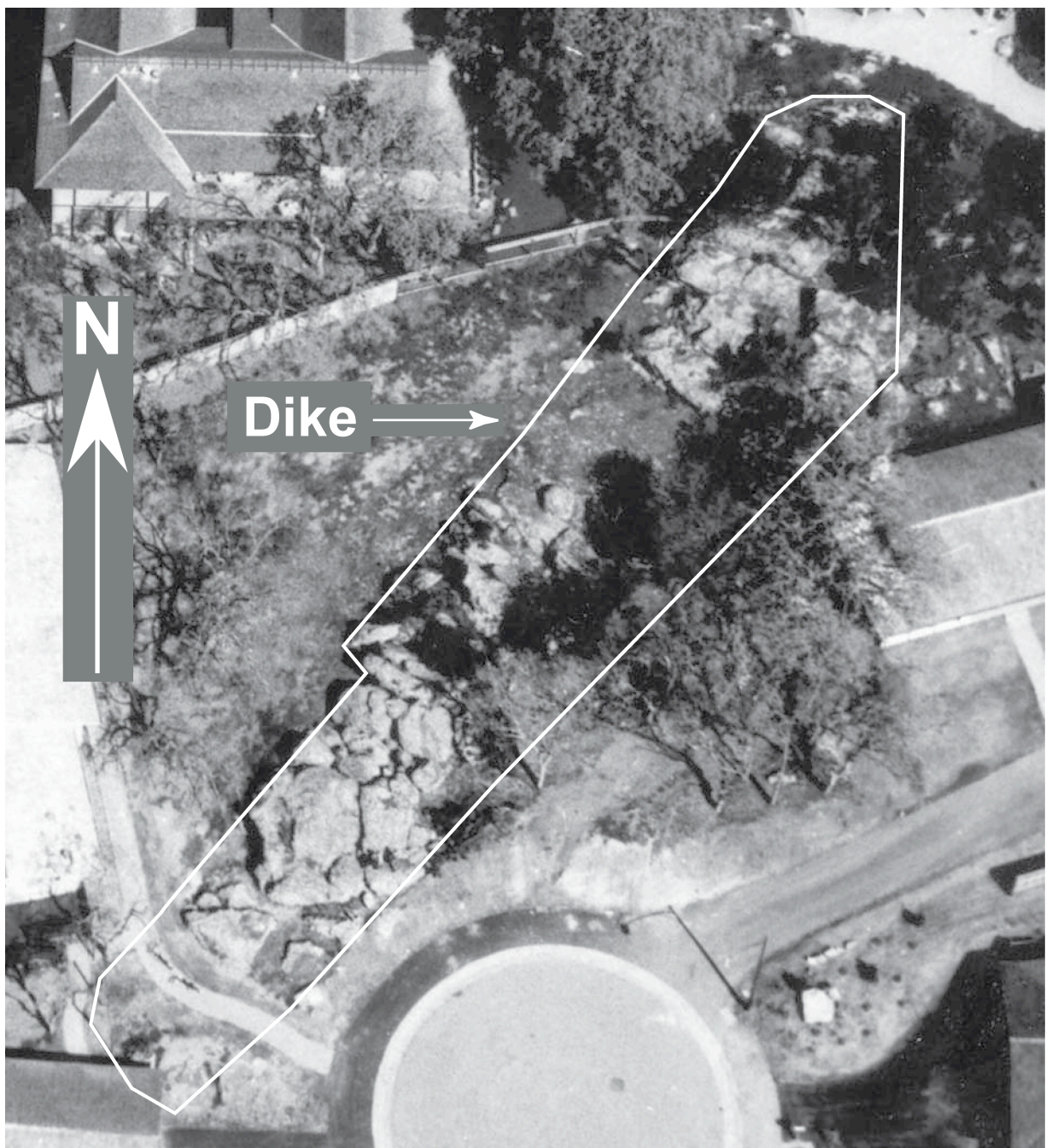


Figure 3. Aerial view of buddingtonite dike, Menlo Park, California. Note the blocky nature of dike. Dike outcrop is 58 m long. (Photo by Norm Prime, USGS, 1964.)

Tables

Table 1. Minerals noted in buddingtonite dike rock, Menlo Park, California

[Thin section of specimen 335C (Eocene sandstone inclusion in dike rock): Some seams (filled fractures) of moderate yellow (5Y7/6) jarosite or buddingtonite. Traces of HgS in the rock, commonly in fractures containing jarosite-buddingtonite, though some feldspar grains were altered and/or replaced by NH₄ minerals and HgS. Quartz overgrowths on quartz and feldspar(?); on quartz are in optical continuity, but on feldspar(?) as rims with different extinction angles and refractive index. Honey-colored crystalline material in holes is ammoniojarosite as hexagonal planes. Also contains what appear to be zircon shells(?) and pleochroic green tourmaline(?).]

Mineral	Chemical Formula	Notes
Buddingtonite	NH ₄ AlSi ₃ O ₈ ·1/2 H ₂ O	Amorphous material
Cinnabar	HgS	On and in quartz and jarosite
Pyrite and Marcasite(?)	FeS ₂	Streaked-out aggregates parallel to flow banding (and bedding in breccia fragments)
Pyrrhotite(?)	FeS	Crystals(?) and negative crystals in buddingtonite
Gypsum*	CaSO ₄ ·H ₂ O	In fractures
Niter*	KNO ₃	
Anatase	TiO ₂	In x-ray diffraction patterns
Hydrocarbons, oily	C _x H _x	In quartz-lined vugs in siliceous breccia
Ammoniojarosite	(NH ₄) ₂ Fe ₆ (OH) ₁₂ (SO ₄) ₄	Honey-colored material as hexagonal plates in vugs and fracture fillings and adjacent to fractures
Jarosite(?)	K ₂ Fe ₆ (OH) ₁₂ (SO ₄) ₄	
Chalcopyrite(?)	CuFeS	Iridescent brass-colored grains
Limonite	2Fe ₂ O ₃ ·3H ₂ O	
Alunite*	KAl ₃ (SO ₄) ₂ (OH) ₆	
Covellite(?)	CuS	Iridescent gray metallic grains
Carnotite*	K ₂ (UO ₂) ₂ (VO ₄) ₂ ·3H ₂ O	Small green crystals in buddingtonite
Ammonium muscovite	(NH ₄) ₂ O·Al ₂ O ₃ ·SiO ₂ ·2/3H ₂ O	

*Determined by R.C. Erd

Table 2. - Distribution of ammonia in samples from the Palo Alto quadrangle and vicinity
[+++ , NH₄ abundant; +, NH₄ present; -, NH₄ not detected]

Locality (see figures 1 and 2)	Sample description	NH ₄ test*	Ammonium minerals determined by x-ray diffraction
<i>Palo Alto 7½' quadrangle:</i>			
1. Sunset Court, Menlo Park	Altered rhyolitic dike rock	+++	Buddingtonite, ammoniojarosite, clay minerals
	Silicified breccia of dike rock and wall rock	+++	Buddingtonite, ammoniojarosite
2. Sharon Park Drive, Menlo Park	Hard, feldspathic sandstone	+++	Buddingtonite, montmorillonite
3. Saga Foods building site, Menlo Park	do.	+++	do.
4. Road cut, Sand Hill Road, Menlo Park	Soft, expansive, gypsum-bearing Eocene claystone	+	Montmorillonite, buddingtonite
5. St. Denis Church parking area, Menlo Park	do.	+	Montmorillonite, traces of buddingtonite
6. Mesa Court, Atherton	do.	+	Montmorillonite, illite(?)
7. Stockbridge Ave, Atherton	Expansive, bleached, gypsum-bearing claystone spoil from basement excavation (Eocene)	+++	Montmorillonite, traces of buddingtonite
8. Harvard Court, Palo Alto	Diatomaceous vitric tuff (Miocene)	+++	n = 1.502 glass containing NH ₄
9. Construction site on Sand Hill Road	Clayey, fine-grained sandstone in test boring (Mid- Miocene)	+	Montmorillonite
<i>Mount Diablo mine area:</i>			
Mercury prospect ½ mile east of main mine workings	Altered (Tertiary) rhyodacite plug	+	Sericite(?)
#6 Bench, east end of main open cut	Bleached graywacke fragments in old landslide debris overlying main quick-silver deposit	+	Plagioclase feldspars and clay minerals
<i>New Almaden district:</i>			
Lone Hill quarry, San Jose	Altered pyroclastic tuff, perlite dacite, and vesicular dacite (Miocene)	-	---
West edge of Almaden Country Club, San Jose	Strongly altered dacitic rock (Miocene)	-	---

*Closed-tube test described by Erd and others (1964, p. 842).